Championing stochastic electronic structure methods with CHAMP

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1 Quantum Monte Carlo

Stochastic solution to the interacting Schrödinger equation

Why (real-space) quantum Monte Carlo (QMC)?

- Favorable scaling! Energy is $O(N^4)$
- Flexibility in the choice of the functional form of the wave function
- Easy parallelization
- Among most accurate calculations for medium-large systems

Simplest flavor of QMC: Variational Monte Carlo (VMC)

Quantum Observables → Expectation Values → Integrals

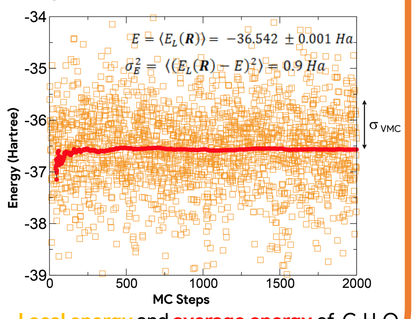
$$E = \frac{\langle\Psi|\mathcal{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \int d\mathbf{R}^{3N} \frac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \frac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R}^{3N}|\Psi(\mathbf{R})|^2}$$

Probability density

$$\approx \frac{1}{M}\sum_{i=1}^{M} E_L(\mathbf{R}_i)$$

← Sampled by Metropolis

Random walk in 3N dimensions, $\mathbf{R} = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$



Local energy and average energy of C_3H_6O

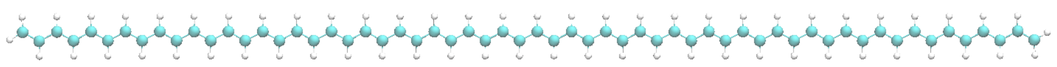
2 CHAMP

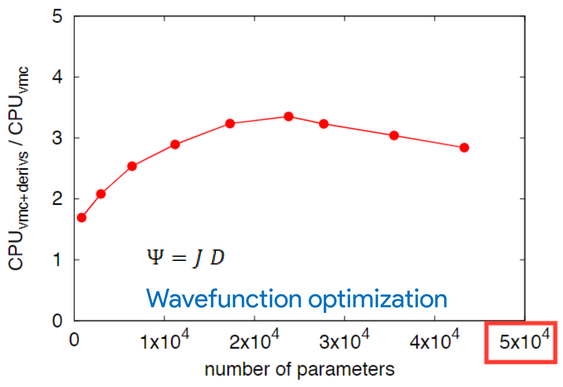
- ★ Efficient algorithms for VMC and DMC
- ★ Fast computation of derivatives of energy and multideterminant expansions
- ★ Wave function and structural optimization for ground and excited states
- ★ Multiscale approaches: QMC/(PCM, MM, MMpol)

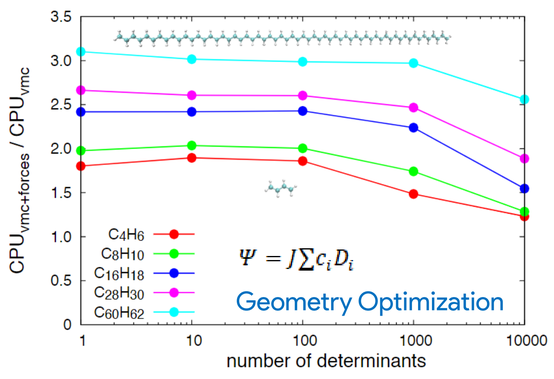
3 Efficient Derivatives of Energy

Wave function and structure optimization

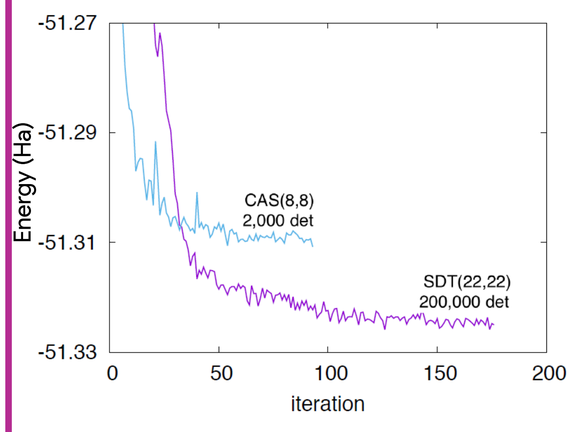
(Cost of VMC + forces)/ (cost of VMC) for polyenes C_4H_6 to $C_{60}H_{62}$



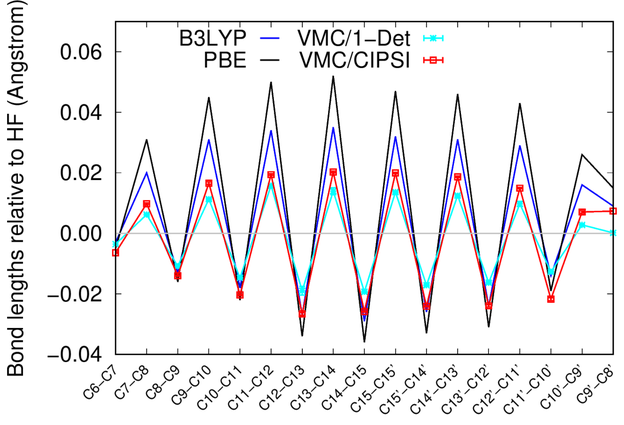




Combining both optimizations (wave function + geometry)



65000 wave function parameter optimization of C_8H_{10}



Bond length variation with respect to HF

Octatetraene

Piridinine

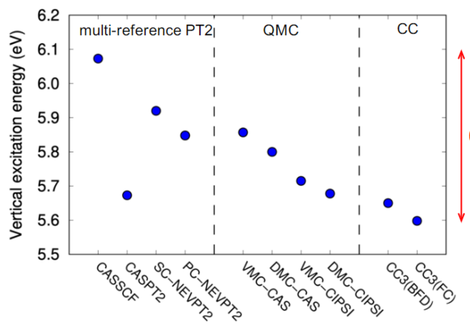
Acknowledgements

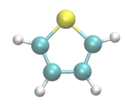
TREX Targeting Real chemical accuracy at the EXascale

4 Excited States

Accurate prediction of excited states can be very challenging.

Vertical excitation energy of thiophene





"Simple" single excitation calculation and ...

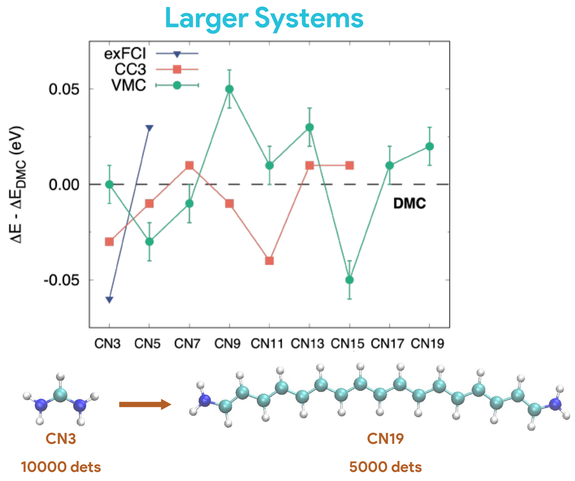
these are all correlated methods!

Not an unusual situation!

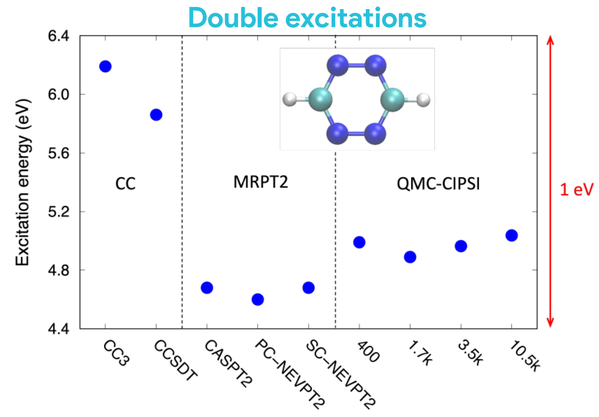
In CHAMP: State-specific optimization in excited states with sophisticated wave

→ We provide a benchmark when other methods "fail"

Larger Systems

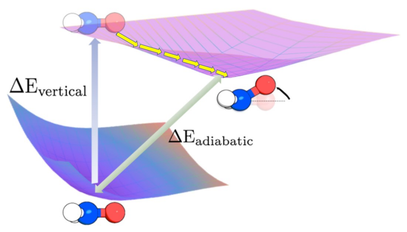


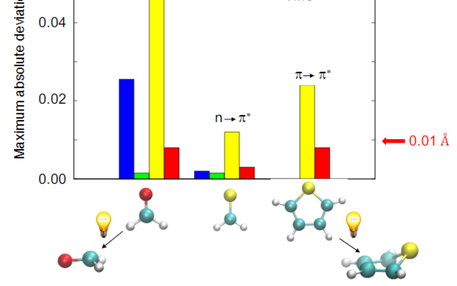
Double excitations



We provide benchmark where other correlated methods struggle (either because of size or correlation level)

In CHAMP: We can also follow structural relaxation in excited states





5 Towards Exascale

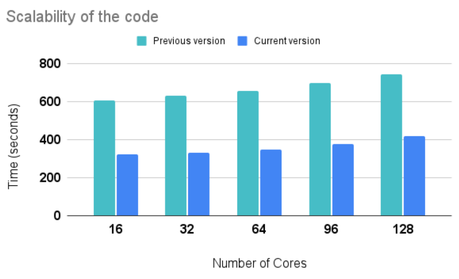
1 Exa = 10^{18} floating point operations per second

Upcoming Exascale Supercomputers in EU

QMC is advantageous for being massively parallel, requiring small I/O and little communication

CHAMP code is currently improving its performance

- Memory access
- Compiler flags (inlining, align, fused-multiply-add)
- AVX512 vectorization instructions
- Loop restructuring (removal of low-count loops, non-conditional loop limits)

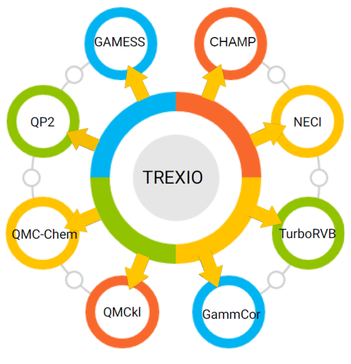


Within the TREX-CoE, we are developing high-performance libraries.

Also visit poster B4.10

TREXIO

Input/Output library for universal data exchange among QC/QMC codes



QMCkl

Core QMC kernel library for highly -efficient, optimized, scalable, common QMC tasks

Get libraries from GitHub